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Piezochromic Polymer Materials Displaying Pressure Changes in Bar-Ranges

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Abstract A piezochromic material exhibiting a pressure dependent reversible shift of the selective reflection wavelength via the entire visible range is developed. The material consists of a cholesteric mixture embedded in a cholesteric elastomer matrix bearing mesogenic side chains with similar molecular structure. The change of the selective reflection has its origin in a compressible helix structure. Thus, the pitch length is switched by pressure changes. To trigger the reversible piezochromic effect already pressure changes in bar-range are sufficient. The pressure controlled colour changes are excellent detectable by the human eye and still appear even after 100 cycles.

Keywords Piezochromic, Polymer, Selective Reflection, Pressure Sensor, Ordered Structure

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1. Introduction

Piezochromic effects based on modification changes of inorganic crystalline materials, such as LiF or NaCl monocrystals, are known phenomena since several decades. For example, the transition from the green α- into the red γ-modification of $CuMoO_4$ requires a pressure of 2.5 kbar and transitions in palladium complexes are reported to require pressures ranging from 1.4 to 6.5 GPa (=14 to 65 kbar)[1,2]. However, the high pressure which is necessary for the modification changes makes these materials unsuitable as pressure sensors in the ordinary area of life. Colour changes by pressure in organic polymer materials are frequently but not systematically described in literature so far. A bathochromic shift of the absorption band of poly (3-dodecylthiophene) was observed by increasing the pressure from atmospheric pressure to 8 kbar[3]. In reference[4] a bathochromic shift from 605 nm to 672 nm ($\Delta\lambda = 67$ nm) is reported for poly[3-(1-dodecyl) thiophene-2,5-diyl] when the pressure is increased from normal pressure to 10.71 GPa (=107.1 kbar). The piezochromic effect of these conjugated polymers is based on pressure dependent shifts of the absorption band. The aim of the present work was to develop piezochromic polymer materials exhibiting, for the first time, colour changes detectable with the human eye in dependence of pressure differences as small as a few bar. Such material could be used as an optical pressure sensor in the ordinary area of life. Our strategy is based on the knowledge about the preparation of cholesteric polymer materials with a selective reflection in the visible range[5-8] and the possibility to tune the helical pitch and thus the selective reflection wavelength by stress[9,10]. The integra-tion of a cholesteric structure in a cross-linked polymer network with soft elastic properties should lead to the aimed piezochromic behaviour. Under pressure an elastic deformation of the helical pitch should appear resulting in a change of the selective reflection colour as shown in Figure 1.

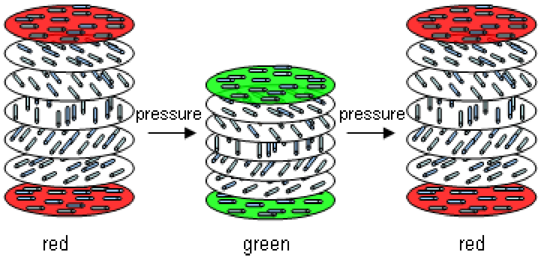

Figure 1. Pressure-dependent changes of the selective reflection wavelength of a helical structure

2. Experimental

All chemicals were purchased from Aldrich and were used without further purification. Cholesterylacrylate (**IV**) was synthesised from cholesterol and acryloylchloride based on a procedure described in[7].

The phase-transition temperatures were determined with a Perkin Elmer DSC7 at a heating rate of 5K / min. An Olympus BH-2 polarizing optical microscope equipped with a Linkam THMSE-600 hot stage was used to observe the phase-transition temperatures and to analyze the liquid-crystalline properties through the observation of the optical textures.

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The photopolymerisation was carried out by exposure with a Black Light lamp (Philips PL-S 9W/08) under Argon for 15 min.

3. Results and Discussion

The investigation was started with an eutectic mixture of different cholesteryl derivatives, which exhibits a cholesteric phase with a selective reflection of red light at room temperature. The mixture is composed of the components cholesteryloleylcarbonate (**I**), cholesterylchloride (**II**) and cholesterylnonanate (**III**) with a ratio of 13.9:32.9:53.2 wt.-%.

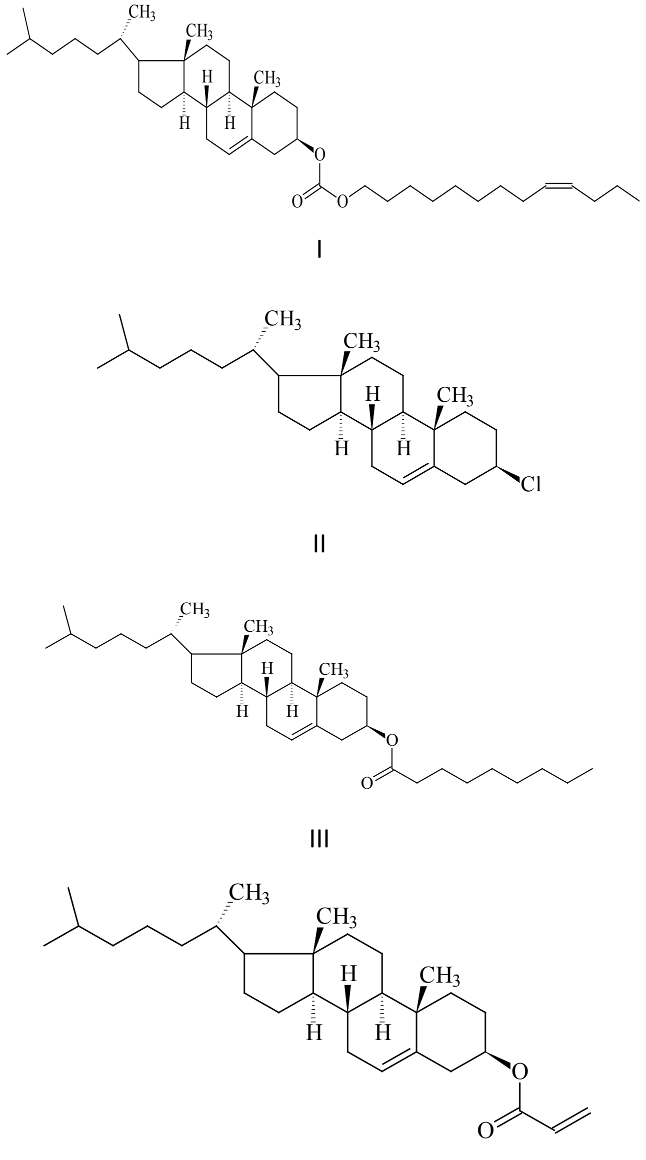
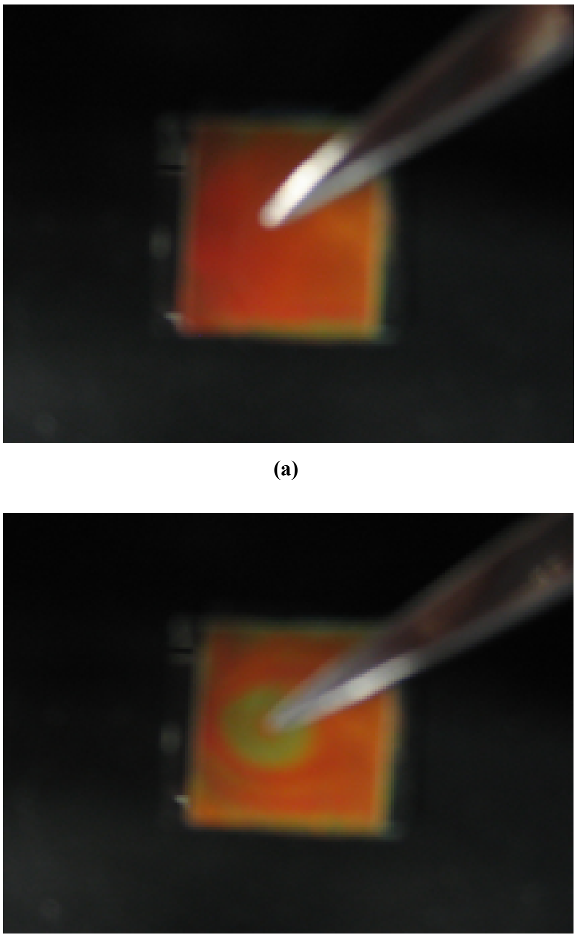


Figure 2. Structure of the used Cholesteryl derivatives **I** – **III** and Cholesterylacrylate **IV**

As determined by DSC measurements and polarising optical microscopy the mixture exhibits a cholesteric phase in between the glass transition temperature of -31.8°C and the clearing temperature of 67.9°C. These results are in accordance to data from the literature[11].

With the intention to obtain a sufficient interaction between the cholesteryl mixture and the elastic polymer matrix as well as to perpetuate the selective reflection behaviour of the cholesteric phase cholesterylacrylate (**IV**) was selected as monomer component. Cholesterylacrylate is added to the eutectic cholesteryl mixture of compounds **I**, **II** and **III** in combination with a cross-linker such as polyethyleneglycol diacrylate and a photo initiator such as Genocure™ LTM (Rahn AG). Afterwards, it was photopolymerised from the cholesteric phase to build up an ordered polymeric network. Note, that it is important to carry out the polymerisation in the cholesteric phase. This is essential to transfer the helical structure into the elastomeric polymer network. An analogous mechanism is discussed in anisotropic gels[12]. The similar structure between the helix component and the matrix is the origin for the form stability of the superior ordered structure of the whole system. In this context, it should be note, that piezochromic luminescence materials are based on a high ordered structure too[13]. The reversible piezochromic behaviour of a prepared elastomer with selective reflection is shown in Figure 3.



(b)

Figure 3. Photos of the piezochromic material mounted between two glass slides. A local change from red (a) to green occurs if an appropriate pressure is applied (b)

The sample shown in Fig. 3 has been prepared by photopolymerisation of a mixture of 21 wt.-% cholesterylacrylate, 77.5 wt.-% of the eutectic mixture of **I-III**, 1 wt.-% polyethyleneglycol diacrylate and 0.5 wt.-% of Genocure™ LTM at room temperature. It has an area of 2.6x2.6 cm and a thickness of 0.1 mm. Over the total sample area a homogeneous selective reflection colour and the same piezochromic properties are observed. Therefore it can be assumed, that a high ordered structure without interruption exist. This is a necessary precondition to transfer the pressure forces from the matrix to the helix with their specific pitch. The reduction of the pitch length by pressure leads to a colour change from red (612 nm) to green (552 nm) if (additionally to normal pressure) a pressure of 0.4 bar is applied in the direction of the helix axis. Only a time less 1 second is needed to trigger between the different colours in dependence on pressure. In order to display the piezochromic effect by spectroscopy an absorbance-wave length plot was carried out (Figure 4).

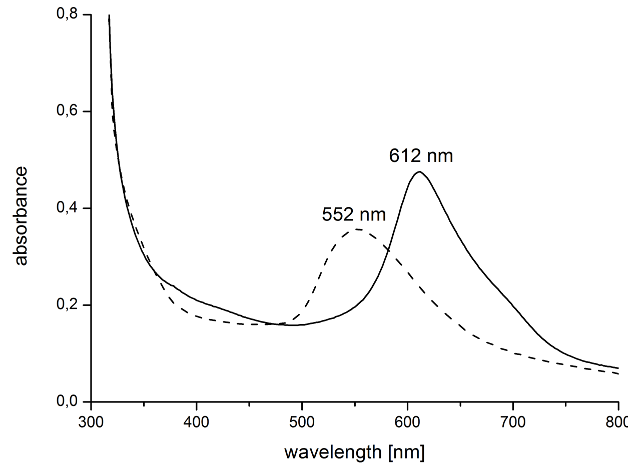


Figure 4. UV/Vis spectra of a piezochromic film without (—) and under (--) pressure of 0.4 bar

It can be seen, that the macroscopic behaviour as shown in Figure 3 is approved. The shift of the reflection maximum in the UV/Vis spectra by applying of pressure is changed from red to green. The difference of approximately 60 nm between the non-pressure and pressure mode is clear detected. Furthermore, it seem that the piezochromic effect possess long time stability. After switching of more than 100 cycles and a storage between room temperature and 45°C no damage of colour exhibit.

4. Conclusions

The results are in agreement with the discussed scheme in Figure 1. The piezochromic effect is reversible and its switching time is in the second range. After 100 switching cycles no visible change of the piezochromic properties was observed.

Compared to the known piezochromic organic materials based on conformational structure changes orders of magnitudes smaller pressure differences are sufficient for an eye detectable piezochromism[3, 4]. The high sensitivity and the low pressure working range of the presented material enable to construct a new kind of piezochromic pressure sensor suitable to display changes in the single-digit bar ranges or less. Furthermore, the combination of piezochromism with other chromogenic properties, especially thermochromic or thermotropic effects, could be lead to novel functional materials[14-17].

The preparation of the presented piezochromic material is not a synthetic challenge and well reproducible.

It can be expected, that other elastomers with helical structures exhibit a similar behaviour, if the interaction between the low molecular mass cholesteric phase and the polymeric backbone is strong enough. Analogous systems could be for example alkoxy- or alkyl- cyanobiphenyls in combination with 4-acryloyloxy-4’-cyanobiphenyl as photopolymerisable monomer and a chiral dopant for the adjustment of the cholesteric pitch.

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